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(54) CERAMIC REFRACTORY FIBROUS MATERIAL

(71) We, THE BABCOCK & WILCOX COMPANY, a corporation organised and existing under the laws of the State of New Jersey, United States of America, of 161 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a fine-grained crystalline product produced from an amorphous ceramic fibrous material and a process for producing such a product. The fibrous material may be of the alumina, silica, and alumina-silica types.

Ceramic fibrous materials have ranged in composition from high purity silica fibers to high purity alumina, with the usual commercial fibers having a general alumina content by weight of from 45% to 77% with a general silica content by weight of 52% to 22%. The commercial fibers will also have extremely small amounts of metallic oxides in the form of contaminants such as iron. Sometimes such small amounts of metallic oxide are deliberately added to attain specific objects in the commercial fibers. Generally speaking, the fibers, as manufactured will contain a major portion of the fibers having diameters in the range of 1 to 10 microns, although submicron and above 10 micron fiber sizes have been produced and used.

Ceramic refractory fibrous materials of the alumina, silica, and alumina-silica type have been used for thermal insulation for many years. The usual fiber is commercially manufactured by a jet of air or steam shattering a stream of molten ceramic with the so formed fibers being collected in bulk form. Ordinarily, the collected bulk fibers are compressed to form fiber blankets or sheets of a preferred bulk density. These ceramic refractory fibers are glassy or amorphous as manufactured.

While the theoretical limit temperature of use of the ceramic fibers will be at the melting temperature of the ceramic fibers, which will be in excess of 3,000°F, it is known that alumina, silica, and alumina-silica ceramic fibers will be converted from an amorphous form to a crystalline form when heated above the devitrification temperature of the particular composition involved. When the blanket or compressed sheet is at a typical use temperature, the fiber will retain a substantially permanent set under compression. When the temperature of use is above the devitrification temperature, the amorphous fiber will be converted to a crystalline form which is subject to degradation due to thermally induced changes in its physical dimensions, or even vibration in the system to which it is applied.

In the interest of material integrity and insulation efficiency, it is clear that a ceramic refractory fiber which resists a permanent set at typical temperatures of use is desirable.

In accordance with the invention, there is provided a fine-grained crystalline product which can be compressed and will return to at least 85 to 90% of its original configuration when the compression force is released, obtained from an amorphous ceramic refractory fiber which is capable of devitrification, by heat treating the refractory fiber at a temperature above its devitrification temperature for a selected period of time producing devitrification of the refractory fiber, the heat treatment being terminated subsequent to formation of the fine-grained crystalline product but prior to the onset of excessive grain growth.

The invention also provides a process for forming a fine-grained crystalline product from an amorphous ceramic refractory fiber, comprising heating the refractory fiber to a temperature in excess of its devitrification temperature for a sufficient time to produce devitrification throughout the refractory fiber, and terminating the heating subsequent to formation of the crystalline product but prior to the onset of excessive grain growth.

The invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a graph of a Differential Ther-

mal Analysis of a Kaowool ceramic refractory fiber material (Kaowool is a Registered Trade Mark);

Figure 2 is a graph of the X-ray Diffraction Intensity of the ceramic refractory fiber material whose graph is shown in Figure 1 prior to the heat treatment described herein; and

Figure 3 is a graph of the X-ray Diffraction Intensity of the same ceramic refractory fiber blanket of Figure 2 after heat treatment above the devitrification temperature shown in Figure 1.

Figure 1 graphically illustrates the definite nature of the devitrification temperature value for a particular material, by means of a Differential Thermal Analysis of the material. As shown, curve 10 indicates the thermal nature of the tested material with increasing temperature. In the course of heating, the amorphous or glassy state of the material is maintained until a temperature specific to the material is reached. Thus, it is to be noted that at about 950°C (1,750°F) a definite relatively large and rapid peak 15 in the exothermic regime is indicated. This exothermic peak 15 denotes a change in the state of the fiber material from an amorphous condition to a crystal structure, and the temperature at which this occurs is termed the devitrification temperature.

While the specific devitrification temperature shown in Figure 1 shows a typical curve developed in testing a Kaowool fiber with a general composition by weight of about 45% alumina and 52% silica, it will be understood the actual devitrification temperature value will be somewhat different for other compositions. However, a definite devitrification temperature value can be found for all alumina, silica, and alumina-silica fibrous materials.

Figure 2 is a graphic representation of the X-ray Diffraction Intensity of the abovementioned Kaowool ceramic refractory fiber, at various angles of incidence, prior to the heat treatment of the material above its devitrification temperature, which with the example shown is about 950°C. The relatively smooth nature of curve 20 with respect to curve 30 of Figure 3 is indicative of the amorphous nature of the fiber material.

Consequently, by heat treating the material of Figure 2 above its devitrification temperature of about 950°C, the expected crystal formation appears on the X-ray Diffraction Intensity curve as sharp intensity peaks. Figure 3 depicts the Diffraction Intensity of the Kaowool fiber material of Figure 2 after heat treating the material to about 950°C—1,000°C for about fifteen minutes. Diffraction Intensity peaks 35 indicate the crystal nature of the once amorphous material.

EXAMPLE

A ceramic refractory fiber blanket, such as an alumina-silica fiber refractory, in particular, Kaowool fiber as sold by The Babcock & Wilcox Company, is heat treated in a muffle furnace. This particular fiber blanket has a density of about eight pounds per cubic foot and a devitrification temperature of about 950°C.

Because of the insulation properties of such a fiber material, in order to ensure devitrification throughout the entire blanket and to compensate for the cyclic nature of the furnace, that is, the furnace does not hold a set temperature exactly but cycles above and below that temperature, a temperature greater than the devitrification temperature of the fiber material is used to ensure devitrification throughout the material. Typically, exposure to a temperature of about 1,000°C for about twenty minutes produces the fine-grained crystalline structure required to resist a permanent set deformation. X-ray examinations indicate that the average crystalline size in the fine-grained alumina-silica fiber is less than 200 angstroms (Å). Size < 200 A°

Although tests indicate that heating at temperatures up to about 1,050°C for a period of up to thirty minutes does not impair the deformation resistance of the material, care must be exercised to limit the heat treatment, especially at temperatures above 1,050°C, in order to prevent excessive grain growth, for the use of an excessive temperature above the devitrification temperature, or use of a sufficient devitrification temperature held for an excessive period of time, will tend to produce a coarse-grained structure with poor handling properties.

Samples of ceramic refractory fiber blanket (Kaowool fiber) with a devitrification temperature of about 950°C were subjected to average temperatures ranging from about 950°C to about 1,050°C for selected periods of time varying from ten minutes to one hour. These heat-treated ceramic fibers, formed as blankets of one inch nominal thickness, were then compressed, by a restraining bracket, to 70% of their initial thickness or to 0.7 inches and then exposed to a temperature of about 815°C for 18 hours. These conditions were imposed to simulate use as [illegible]ion for 18 hours at the expected temperature and compression in a gas cooled nuclear reactor. Upon completion of the 18 hour test, the nominal thickness for each of uncompressed material thickness for each of the heat treated ceramic refractory fibrous blankets were as follows

TABLE I

Nominal Thickness (Inches) After 18 Hours at 815°C

Heat Treatment Time ~Min.	Heat Treatment Temp. ~°C 950	980	1,010	1,050
10	.72	.96		.82
	.71	.92		.78
15		.85		.76
		.97		.81
		.80		.81
25	.89	1.02	.82	1.00
	.84	1.01	.79	.98
	.88	1.03		
	.86			
30				1.00
				1.00
60	.83			

Due to the fluffy nature of the fiber blankets, the thickness varies along the dimensions of the blanket and, therefore, is termed a "nominal" thickness.

It will be noted from the above table that it is desirable, under the time schedule indicated, to utilise a temperature of about 30°C to 100°C above the devitrification temperature, of the specific fibrous material treated, to effectively heat treat the material to provide the desired resiliency of the material, which is denoted by a return of about 85% to 90% of the original uncompressed fiber thickness, after release of the compression force.

Ceramic refractory fibrous materials will devitrify when subjected in use to a temperature exceeding the devitrification temperature, and a temperature of use which is significantly above the devitrification temperature will lead to increased crystal growth, resulting in a coarse-grained structure which as mentioned above will have poor handling properties. Therefore, to retain the improved resiliency of the ceramic product, produced by the above-described heat treatment, the product will have a limit temperature of use which is below the devitrification temperature of the fiber material so that heat-induced grain growth will not adversely affect the mechanical or handling properties of the material.

The above-described crystalline products according to the invention have an improved ability to resist a permanent set, in comparison with that which heretofore has been available, and some ceramic fiber material treated by the process of the invention has shown significantly greater resistance to a permanent set or deformation, at elevated temperatures below the divitrification temperature, than the untreated material, and upon compression, returns to at least 85% to 90% of its original dimension when the compression force is released.

WHAT WE CLAIM IS:—

1. A fine-grained crystalline product which can be compressed and will return to at least 85 to 90% of its original configuration when the compression force is released, obtained from an amorphous ceramic refractory fiber which is capable of devitrification, by heat treating the refractory fiber at a temperature above its devitrification temperature for a selected period of time producing devitrification of the refractory fiber, the heat treatment being terminated subsequent to formation of the fine-grained crystalline product but prior to the onset of excessive grain growth.

2. A fine-grained crystalline product according to claim 1 when obtained from an amorphous alumina-silica ceramic refractory fiber.

3. A fine-grained crystalline product according to claim 1 or claim 2 which has a limit temperature of use, which is below the devitrification temperature of the refractory fiber.

4. A fine-grained crystalline product substantially as hereinbefore described in the Example.

5. A process for forming a fine-grained crystalline product from an amorphous ceramic refractory fiber, comprising heating the refractory fiber to a temperature in excess of its devitrification temperature for a sufficient time to produce devitrification throughout the refractory fiber, and terminating the heating subsequent to formation of the crystalline product but prior to the onset of excessive grain growth.

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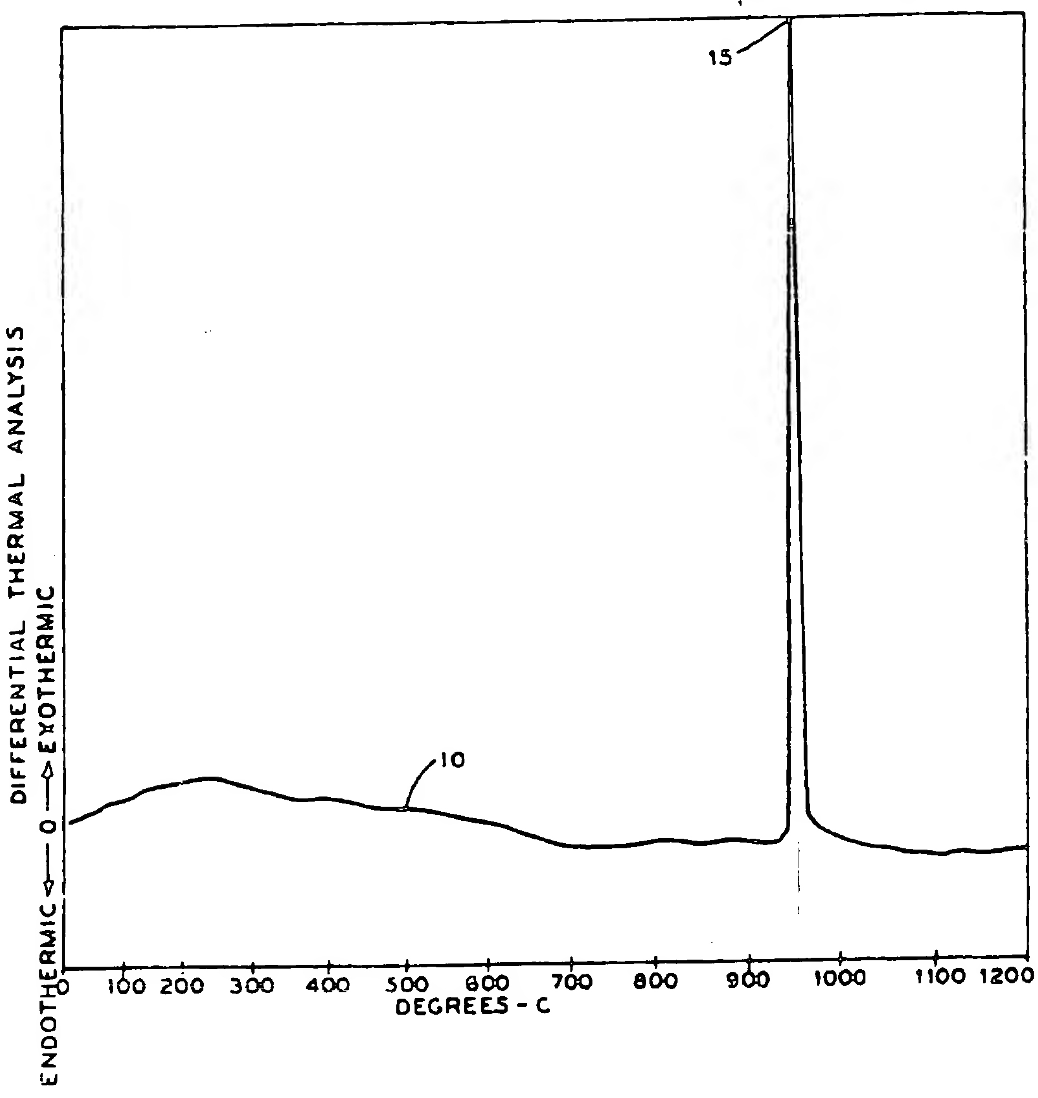
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

peak showing change from amorphous to crystal.



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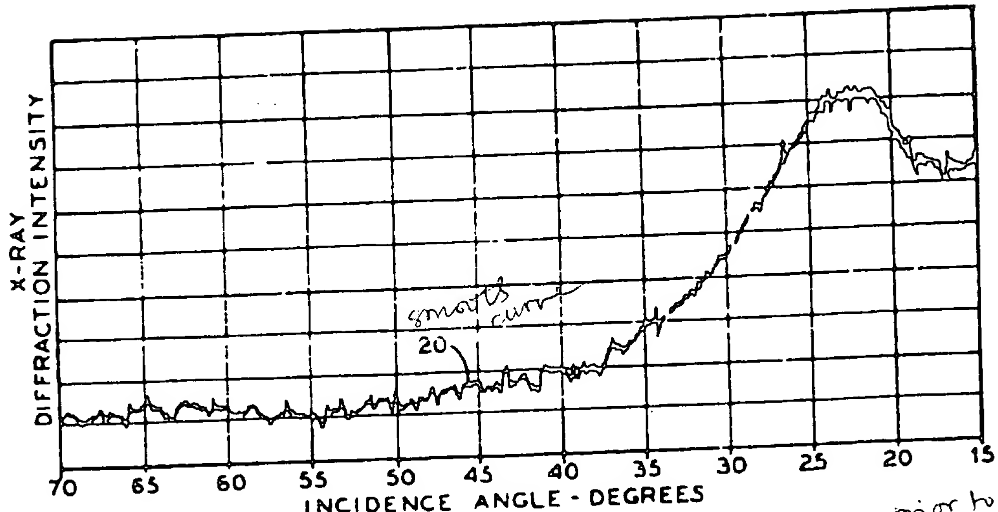
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

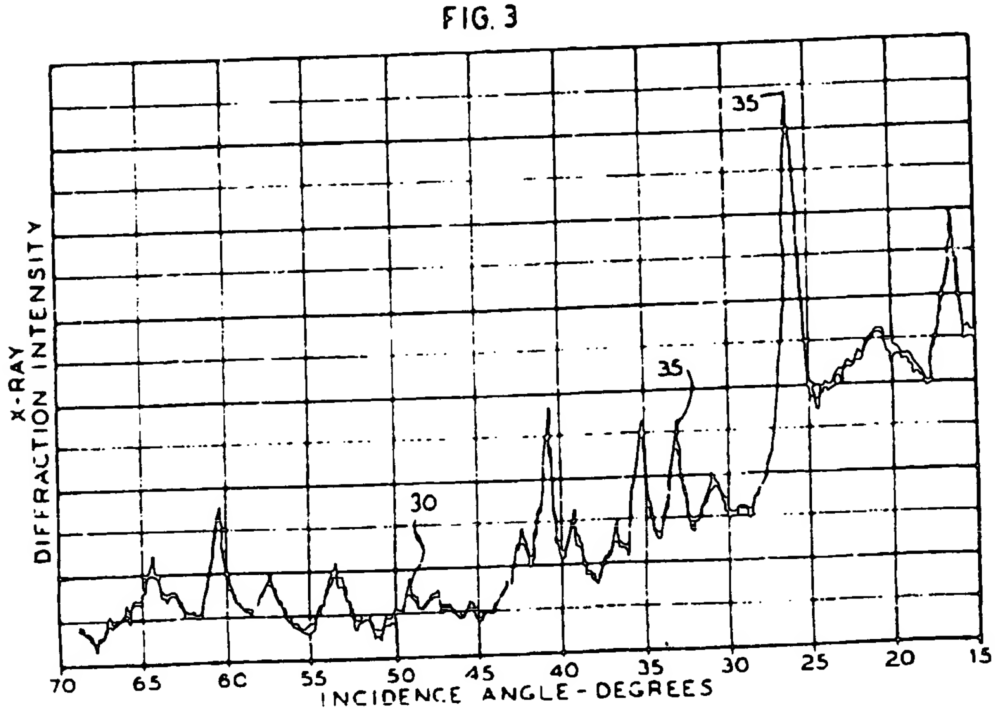
FIG.2



amorphous nature

prior to heat treatment

FIG. 3



crystal nature

after heat treatment @ 950 - 1000°C for 15' min